

Articles

Platinum-Catalyzed Reaction of Alkynes with ArI (Ar = aryl and thienyl) and Ar'SM (M = Na, K, and Sn(Bu-*n*)₃): Three- vs Two-Component Cross-Coupling Reaction

Hitoshi Kuniyasu,* Fumikazu Yamashita, Takayoshi Hirai, Jia-Hai Ye, Shin-ichi Fujiwara, and Nobuaki Kambe

Department of Molecular Chemistry & Frontier Research Center, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

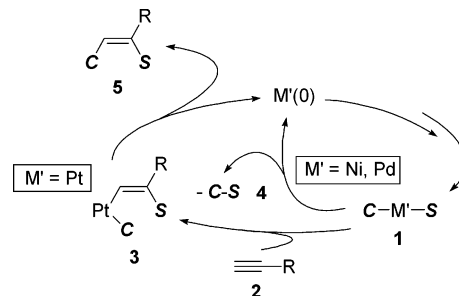
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The Pt-catalyzed reactions of terminal alkynes HCCR (**2**) with ArI (**6**) (Ar = aryl and thienyl) and Ar'SM (M = Li, Na, K, and Sn(*n*-Bu)₃) (**7**) have been examined. Among them, the combined use of 2- and 3-iodothiophene with PhSK resulted in the formation of (*Z*)-Ar(H)C=C(SAr')(R) (**5**) in moderate to good yields. When aryl iodide was employed as a coupling partner, thioether ArSAr' (**4**), a direct cross-coupling product between **6** and **7**, was competitively produced together with **5**. The ratios of formation of **5/4** were significantly dependent on the substituent in Ar of **6** and Ar' of **7** as well as species of **2**. The mechanistic study indicated that **4** was produced by the alkyne-participated reaction of **6** with Pt(Ar')(SAr')(PPh₃)₂ (**1**).

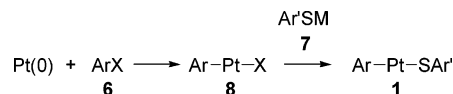
Introduction

Transition metal-catalyzed cross-coupling reactions have served as powerful strategies to build up desired chemical compounds. Along with numerous C–C bond-forming reactions,¹ C–S bond formations have also been developed.^{2,3} On the other hand, we have recently reported on a very simple prototype for achievement of a three-component coupling reaction that enabled the regio- and stereoselective introduction of carbon and sulfur functionalities into terminal alkynes. The basic concept is shown in Scheme 1.⁴ The generation of platinum complex **1** having a C–Pt–S moiety resistant to C–S bond-forming reductive elimination patterned after the Ni- or Pd-catalyzed syntheses of thioethers **4** sets up the reaction.² Then *cis*-insertion of HCCR (**2**) into the Pt–S bond of **1** with Pt bound at the terminal position affords the vinyl platinum complex **3**, possessing a C–Pt–C fragment, and finally C–C bond-forming reductive elimination of vinyl sulfide **5** completes one catalytic cycle to regenerate the Pt(0) complex. According to this working hypothesis, the Pt-catalyzed arylthiolation with aryl thioester,^{5a}

Scheme 1. Strategy for Carbothiolation of Alkyne (**2**)



Scheme 2. Methodology of Generation of **1**



thienylthiolation with thienyl thioester,^{5b} pyridylthiolation with iodopyridine and ArSK,^{5c} and furylthiolation with furyl thioester^{5d} of **2** have been realized gratifyingly.

Herein we wish to report on details about carbothiolation using ArX (Ar = aryl and thienyl; X = Cl, Br, I, and OTf) (**6**) and Ar'SM (M = Li, Na, K, and Sn(Bu-*n*)₃) (**7**) as the sources of formation of platinum intermediate **1** (M' = Pt) via oxidative addition of **6** to Pt(0) to yield the Pt(II) complex Ar–Pt–X (**8**) and subsequent transmetalation with **7** (Scheme 2).⁶

Results and Discussion

Arylthiolation or Thienylthiolation vs Cross-Coupling Reaction (Table 1). First, the arylthiolation of 1-octyne (**2a**,

(5) (a) Sugoh, K.; Kuniyasu, H.; Sugae, T.; Ohtaka, A.; Takai, Y.; Tanaka, A.; Machino, C.; Kambe, N.; Kurosawa, H. *J. Am. Chem. Soc.* **2001**, 123, 5108. (b) Hirai, T.; Kuniyasu, H.; Kambe, N. *Chem. Lett.* **2004**, 33, 1148. (c) Hirai, T.; Kuniyasu, H.; Kambe, N. *Tetrahedron Lett.* **2005**, 46, 117. (d) Hirai, T.; Kuniyasu, H.; Terao, J.; Kambe, N. *Synlett* **2005**, 7, 1161.

(6) An example of arylthiolation of 1-octyne using PhI and PhSNa has already been reported in a communication (ref 5a).

* To whom correspondence should be addressed. E-mail: kuni@chem.eng.osaka-u.ac.jp.

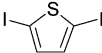
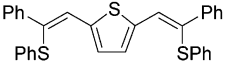
(1) *Metal-catalyzed Cross-coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: New York, 1998.

(2) (a) Kosugi, M.; Shimizu, T.; Migita, T. *Chem. Lett.* **1978**, 13. (b) Murahashi, S.; Yamamura, M.; Yanagisawa, K.; Mita, N.; Kondo, K. *J. Org. Chem.* **1979**, 44, 2408. (c) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kato, Y.; Kosugi, M. *Bull. Chem. Soc. Jpn.* **1980**, 53, 1385. (d) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, 58, 3657. (e) Carpita, A.; Rossi, R.; Scamuzzi, B. *Tetrahedron Lett.* **1989**, 30, 2699. (f) Cristau, H. J.; Chabaud, B.; Chene, A.; Christol, H. *Synthesis* **1981**, 892. (g) Takagi, K. *Chem. Lett.* **1987**, 2221. (h) Deardorff, D. R.; Linde, R. G.; Martin, A. M.; Shulman, M. J. *J. Org. Chem.* **1989**, 54, 2759. (i) Martinez, A. G.; Barcina, J. O.; de Fresno, C. A.; Subramanian, L. R. *Synlett.* **1994**, 561. (j) Rane, A. M.; Miranda, E. I.; Soderquist, J. A. *Tetrahedron Lett.* **1994**, 35, 3225. (k) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, 250, 551. (l) Cristau, H. J.; Chabaud, B.; Labaudiniere, R.; Christol, H. *Organometallics* **1985**, 4, 657. (m) Dickens, M. J.; Gilday, J. P.; Mowlem, T. J.; Widdowson, D. A. *Tetrahedron* **1991**, 47, 8621.

(3) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, 100, 3205.

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Table 1. Carbothiolations of 2 with ArX (6) and Ar'YM' (7)

$\text{R}-\text{C}\equiv\text{C}-\text{R}' + \text{ArX} + \text{Ar'YM'} \xrightarrow{\text{cat. Pt}} \text{Ar}-\text{C}(\text{R})=\text{C}(\text{R}')-\text{YAr'} + \text{ArYAr'}$					
entry	2	6	7 (Y = S, Se)	5 ^b	4 ^b
1	$\text{C}_6\text{H}_{13-n}$ (2a)	PhCl (6a)	PhSNa (7a)	0% (5a)	0% (4a)
2	2a	PhBr (6b)	7a	0% (5a)	0% (4a)
3	2a	PhI (6c)	7a	83% (5a)	3% (4a)
4	2a	PhOTf (6d)	7a	40% (5a)	0% (4a)
5	2a	6c	PhSK (7b)	87% (5a)	5% (4a)
6 ^c	2a	6c	PhSLi (7c)	3% (5a)	9% (4a)
7	2a	6c	PhSSn(Bu- <i>n</i>) ₃ (7d)	66% (5a)	25% (4a)
8	2a	<i>p</i> -MeC ₆ H ₄ I (6e)	7a	63% (5b)	4% (4b)
9	2a	<i>p</i> -CF ₃ C ₆ H ₄ I (6f)	7a	69% (5c)	15% (4c)
10	2a	6c	<i>p</i> -MeC ₆ H ₄ SNa (7e)	52% (5d)	25% (4b)
11	2a	6c	<i>p</i> -MeOC ₆ H ₄ SNa (7f)	36% (5e)	42% (4d)
12	2a	6c	<i>p</i> -CF ₃ C ₆ H ₄ SNa (7g)	72% (5f)	0% (4c)
13	2a	6e	<i>p</i> -MeOC ₆ H ₄ SNa (7f)	53% (5g)	35% (4e)
14	$(\text{CH}_2)_2\text{CH}(\text{CH}_3)_2$ (2b)	6c	7b	69% (5h)	27% (4a)
15	$(\text{CH}_2)_3\text{CN}$ (2c)	6c	7b	58% (5i)	25% (4a)
16	$(\text{CH}_2)_4\text{OH}$ (2d)	6c	7b	60% (5j)	24% (4a)
17	Ph (2e)	6c	7b	30% (5k)	66% (4a)
18 ^d	SiMe ₃ (2f)	6c	7b	12% (5l)	64% (4a)
19	Si(<i>i</i> -Pr) ₃ (2g)	6c	7b	0% (5m)	<1% (4a)
20	2a	 6g	7b	0% (5n)	0% (4f)
21	2a	 6h	7b	72% (5n)	0% (4f)
22	2a	 6i	7a	51% (5n)	0% (4f)
23	2a	6i	7b	98% (5n)	0% (4f)
24 ^e	2a	6i	7c	3% (5n)	0% (4f)
25 ^f	2a	6i	7b	59% (5n) (<i>E/Z</i> = 16/84)	6% (4f)
26 ^{f,g}	-	6i	7b	-	93% (4f)
27 ^h	2e	 6j	 7b	54% (5o)	
28	2a	 6k	7b	80% (5p)	0% (4g)
29	2c	6i	7b	75% (5q)	< 1% (4f)
30	2d	6i	7b	55% (5r)	0% (4f)
31	2e	6i	7b	86% (5s)	7% (4f)
32	$\text{C}_6\text{H}_4\text{OMe-}p$ (2h)	6i	7b	82% (5t)	0% (4f)
33	$(\text{CH}_2)_2\text{OTHP}$ (2i)	6i	7b	57% (5u)	0% (4f)

^a 2 (1.2 mmol), 6 (1.0 mmol), 7 (1.1 mmol), Pt(PPh₃)₄ (0.05 mmol), and toluene (0.5–1.0 mL) under reflux for 24 h. ^b Isolated yield. ^c CH₂=C(SPh)(C₆H_{13-n}) was produced in 62% yield. ^d 2.5 mmol of 2d in a sealed tube at 110 °C. ^e CH₂=C(SPh)(C₆H_{13-n}) was produced in 59% yield. ^f Pd(PPh₃)₄. ^g Without 2a. ^h 7b (2.2 mmol) and 2e (2.4 mmol).

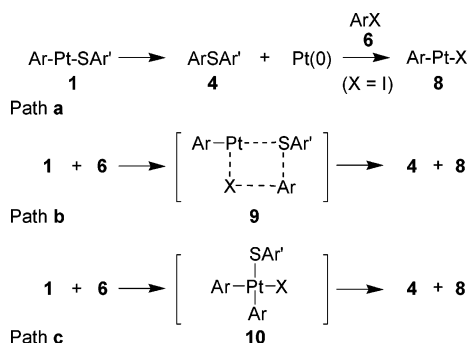
1.2 mmol) was examined using PhX (6, 1.0 mmol) and PhSM (7, 1.1 mmol) in the presence of Pt(PPh₃)₄ (0.05 mmol) under vigorous toluene reflux for 24 h. Both reactions using PhSNa (7a) with PhCl (6a) and with PhBr (6b) did not produce arylthiolation products (entries 1 and 2), while the reactions using PhI (6c) and PhOTf (6d) gave the anticipated (Z)-Ph-(H)C=C(SPh)(C₆H_{13-n}) (5a) in 83% and 40% yields, respectively (entries 3 and 4).^{2a,c}

The reaction of 6c with PhSK (7b) also provided 5a in 87% yields (entry 5); however, the reaction using PhSLi (7c) produced only 3% of 5a and the hydrothiolation product CH₂=C(SPh)(C₆H_{13-n})⁷ was instead obtained in 62% yield (entry 6). The reaction of 6c with PhSSn(Bu-*n*)₃ (7d) yielded 5a in 66% yield (entry 7).^{2d} Interestingly, contrary to the cases of arylthiolation using thioesters,^{5a} PhSPh (4a), a direct cross-coupling product between 6c and 7, can also be furnished under these

reaction systems.⁸ For example, 4a was obtained in 3% and 25% yields when 6c and 7a or 6c and 7d were employed as coupling components (entries 3 and 7). The amount of 4 was significantly influenced by the electronic nature of Ar in 6 and Ar' in 7. The introduction of an electron-withdrawing group in Ar of ArI slightly increased the yield of 4 (entry 9; Ar = *p*-CF₃C₆H₄, 6f, 15% of *p*-CF₃C₆H₄SPh (4c)) compared to the case of Ph (entry 3; 6c, 3% of 4a) or Ar with an electron-donating group (entry 8; Ar = *p*-MeC₆H₄, 6e, 4% of *p*-MeC₆H₄-SPh (4b)). On the other hand, the introduction of electron-donating groups in Ar' of Ar'SNa increased the formation of 4 (entry 10; Ar' = *p*-MeC₆H₄, 7e, 25% of 4b, entry 11; Ar' = *p*-MeOC₆H₄, 7f, 42% of 4d, and entry 13; Ar' = *p*-MeOC₆H₄, 7f, 35% of 4e), while an electron-withdrawing group suppressed the generation of 4 (entry 12; Ar' = *p*-CF₃C₆H₄, 7g, 0% of 4c). The ratios of 5 and 4 also varied with the species of alkyne (2).

(7) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902.

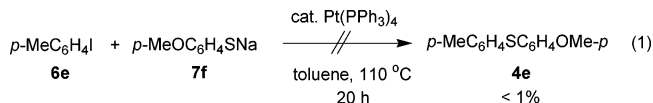
(8) Thioesters were also produced as byproducts under the Pt-catalyzed pyridylthiolation of alkynes by iodopyridine and ArSK. See ref 5c.

Scheme 3. Possible Reaction Routes to the Formation of 4

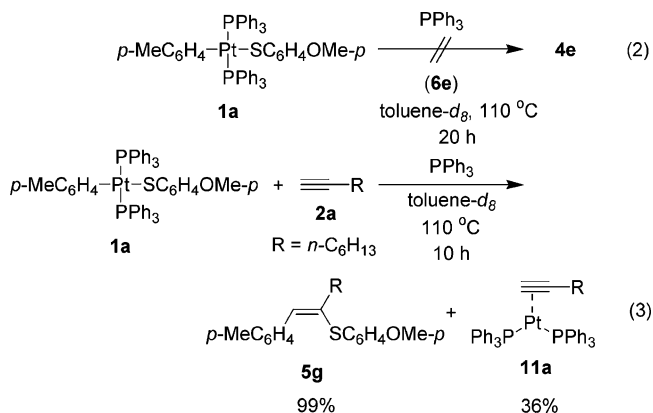
The replacement of **2a** for branched aliphatic terminal alkyne **2b** increased the generation of **4** to furnish 69% of **5h** and 27% of **4a** (entry 14 vs entry 5). The arylthiolation of alkynes having $-\text{CN}$ and $-\text{OH}$ groups also provided the three-component coupling products **5i** and **5j** in moderate yields (entries 15 and 16). When phenyl acetylene (**2e**) and (trimethylsilyl)acetylene (**2f**) were employed, major products were ended in **4a** to yield 30% of **5k** with 66% of **4a** and 12% of **5l** with 64% of **4a**, respectively (entries 17 and 18). Moreover, the formation of **5** and **4** was both totally suppressed when more bulky (triisopropylsilyl)acetylene (**2g**) was employed as the substrate (entry 19), suggesting that the coordination of **2** to the Pt complex must be prerequisite for the formation of thioether (**4**) as well as the production of **5**. Next, the thienylthiolations using ArX and Ar'SM were examined. Although chloride again did not show any activity toward carbodithiolation (entry 20), the reaction employing bromide afforded the desired product **5n** in moderate yield (entry 21). On the other hand, the thienylthiolation of **2a** employing 2-iodothiophene (**6g**) with PhSK (**7b**) more efficiently produced desired product **5n** in 98% yield (entry 23). The potassium thiolate exhibited the highest activity among alkali metals examined (entries 22–24). It is a noteworthy fact that palladium complex ($\text{Pd}(\text{PPh}_3)_4$), which catalyzed the direct cross-coupling reaction between **6g** and **7b** to afford **4f** in good yield (entry 26) and did not catalyze the arylthiolation of alkyne by aryl thioester,^{5a} also possessed catalytic activity for thienylthiolation, albeit in lower yield (59%) and with formation of a mixture of stereoisomers (*E/Z* = 16/84) (entry 25).^{5b} Thiophene derivative **5o**, with a more extended conjugated moiety, was obtained in 54% yield by employing 2,5-diiodothiophene (entry 27). 3-Thienylthiolation by 3-iodothiophene (**6k**) also successfully proceeded to afford **5p** in 80% yield (entry 28). 2-Thienylthiolation was also successfully applied to other terminal alkynes (**2c**, **2d**, **2e**, $\text{HCCCC}_6\text{H}_4\text{OMe-p}$ (**2h**), and $\text{HCC}-(\text{CH}_2)_2\text{OTHF}$ (**2i**)) to give the corresponding three-component coupling products in moderate to good yields (entries 29–33). Again, the formation of **4f**, a direct cross-coupling product between **6i** and **7b**, was fairly suppressed under these thienylthiolations.

Mechanistic Study: Arylthiolation vs Cross-Coupling Reaction. With respect to the formation of direct cross-coupling product ArSAr' (**4**), three reaction routes are conceivable (Scheme 3). Path a showed the C–S bond-forming direct reductive elimination of **4** from Pt(II) complex (**1**) with the regeneration of Pt(0), which can be trapped by **6** ($\text{X} = \text{I}$) to give **8**. The σ -bond metathesis between the Pt–S bond of **1** and the X–Ar bond of **6** via the four-membered intermediate **9** (path b) and reductive elimination via Pt(IV) intermediate **10** formed by the oxidative addition of **6** to **1** (path c) were also possible. Then to get information about the reaction route to **4**, the following reactions were next examined.

First, the Pt-catalyzed cross-coupling reaction between $p\text{-MeC}_6\text{H}_4\text{I}$ (**6e**) and $p\text{-MeOC}_6\text{H}_4\text{SNa}$ (**7f**) was attempted; however, only a trace amount of **4e** (<1%) was detected after 20 h at 110 °C (eq 1).



In good accordance with this fact, heating the toluene- d_8 (0.6 mL) solutions of *trans*- $\text{Pt}(\text{C}_6\text{H}_4\text{Me-p})(\text{SC}_6\text{H}_4\text{OMe-p})(\text{PPh}_3)_2$ (**1a**, 0.01 mmol)⁹ and PPh_3 (0.05 mmol) added as *trans*-to-*cis* isomerization catalyst either in the presence or in the absence of **6e** did not produce $p\text{-MeC}_6\text{H}_4\text{SC}_6\text{H}_4\text{OMe-p}$ (**4e**) at all (eq 2). It should be noted that 35% of **4e** was produced under the reaction of **2a** with **6e** and **7f** (entry 13 in Table 1).



Then the reaction of **1a** with **2a** was monitored by ^1H and ^{31}P NMR spectroscopy (eq 3). After 10 h at 110 °C, the formation of **5g** (99%) and $\text{Pt}(\text{PPh}_3)_2(\text{HCCR})$ (**11a**; 36%) was confirmed;¹⁰ however, **4e** was again not detected at all. It must also be noted that no signal of suspected vinyl platinum **3** (Scheme 1) was detected during the course of the reaction, presumably because the C–C bond-forming reductive elimination¹¹ from **3** was much faster than the insertion of **2** into the Pt–S bond of **1**.

With respect to the C–S bond formation from Pd(II) complexes, Hartwig et al. have disclosed that the introduction of an electron-withdrawing group in the detaching carbon functional group and an electron-donating group in the sulfur functional group promoted the reaction.¹² The electronic effects observed in entries 8–13 of Table 1 apparently accord with the electronic nature of C–S bond formation from Pd(II) complexes. However, the above experimental results indicated that the participation of path a of Scheme 3 for the generation of thioether (**4**) was unlikely under the Pt-catalyzed reaction of alkyne (**2**) with ArX (**6**) and Ar'SM (**7**).¹³

Then to examine the possibility of the participation of both **6** and **2** in the formation of **4**, the reaction of *trans*- $\text{Pt}(\text{C}_6\text{H}_4\text{-$

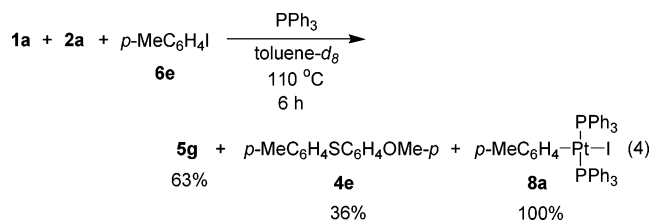
(9) The authentic *trans*-**1**, which was thermodynamically more stable than *cis*-**1**, was successfully prepared by the reaction of $\text{Pt}(\text{PPh}_3)_4$ with ArI then Ar'SNa.

(10) The low yield of **11a** may be attributable to the formation of $\text{Pt}(\text{PPh}_3)_4$, which cannot be detected by ^{31}P NMR spectroscopy due to rapid liberation of PPh_3 in solution.

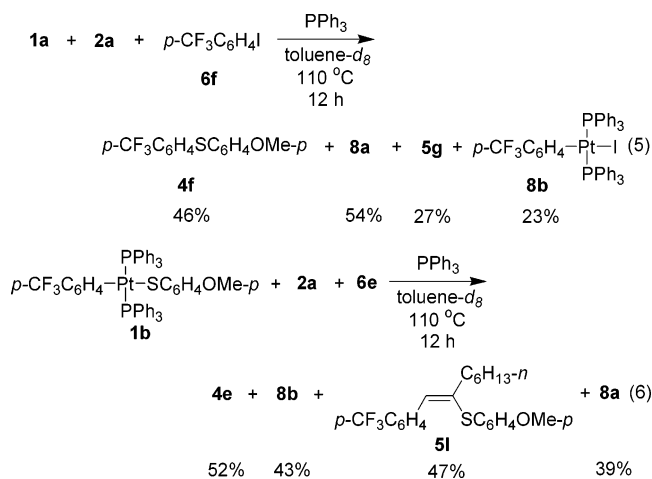
(11) (a) Stang, P. J.; Kowalski, M. H. *J. Am. Chem. Soc.* **1989**, *111*, 3356. (b) Merwin, R. K.; Schnabel, R. C.; Koola, J. D.; Roddick, D. M. *Organometallics* **1992**, *11*, 2972, and references therein.

(12) (a) Mann, G.; Baranano, D.; Hartwig, J. F.; Rheingold, A. L.; Guzei, I. A. *J. Am. Chem. Soc.* **1998**, *120*, 9205. (b) Baranano, D.; Hartwig, J. F. *J. Am. Chem. Soc.* **1995**, *117*, 2937.

Me-*p*)(SC₆H₄OMe-*p*)(PPh₃)₂ (**1a**, 0.01 mmol) with HCCC₆H₁₃-*n* (**2a**) (0.1 mmol) was next performed in the presence of *p*-MeC₆H₄I (**6e**, 0.1 mmol) (eq 4). Contrary to the cases of reactions of **1a** with **6e** (eq 2) and **1a** with **2a** (eq 3), the formation of **4e** (36%) was confirmed after 6 h together with **5g** (63% based on SC₆H₄OMe-*p* of **1a**) and *trans*-Pt(C₆H₄Me-*p*)(I)(PPh₃)₂ (**8a**, 100% based on Pt).



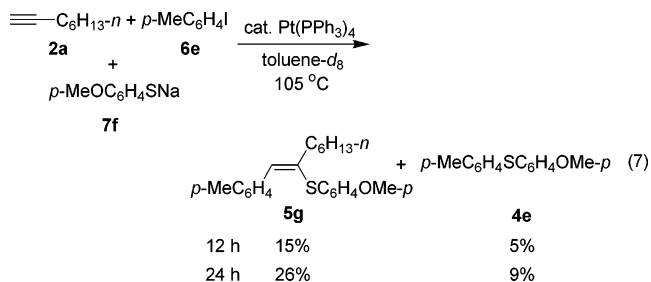
Furthermore, to get insight about the origin of the Ar moiety of Ar-SAr' (**4**), the reaction of **1a** (0.01 mmol) and **2a** (0.03 mmol) with *p*-CF₃C₆H₄I (**6f**, 0.1 mmol) (eq 5) and the reaction of *trans*-Pt(C₆H₄CF₃-*p*)(SC₆H₄OMe-*p*)(PPh₃)₂ (**1b**, 0.01 mmol) and **2a** (0.03 mmol) with *p*-MeC₆H₄I (**6e**, 0.1 mmol) (eq 6) were next examined.



The former produced *p*-CF₃C₆H₄SC₆H₄OMe-*p* (**4f**, 46% based on SC₆H₄OMe-*p* of **1a**) and *trans*-Pt(C₆H₄Me-*p*)(I)(PPh₃)₂ (**8a**, 54% based on Pt) as well as **5g** (27% based on SC₆H₄OMe-*p* of **1a**) and *trans*-Pt(C₆H₄CF₃-*p*)(I)(PPh₃)₂ (**8b**, 23% based on Pt). On the other hand, the latter produced *p*-MeC₆H₄SC₆H₄OMe-*p* (**4e**, 52% based on SC₆H₄OMe-*p* of **1a**) and **8b** (43% based on Pt) as well as **5l** (47% based on SC₆H₄OMe-*p* of **1a**) and **8a** (39% based on Pt). These results clearly showed that the Ar moiety of **4** was selectively derived from newly added **6**. The facts that the yields of **4f** and **8a** as well as **5g** and **8b** in eq 5 and yields of **4e** and **8b** as well as **5l** and **8a** in eq 6 were all comparable with each other did not contradict the assumption that the formation of these compounds also correlated with each other.

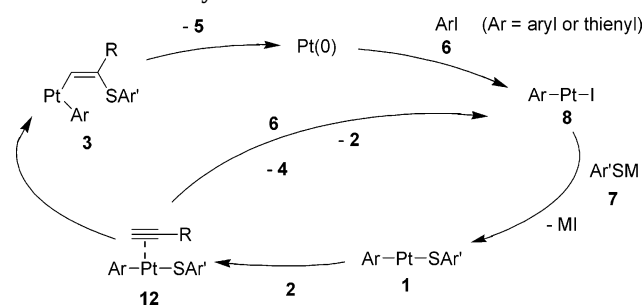
Foregoing data may suggest the involvement of path b of Scheme 3 for the formation of **4**, because the increase of electrophilicity of **6** by introducing an electron-withdrawing group (entry 9 in Table 1) and the increase of nucleophilicity of the SAR' moiety in **1** by introducing electron-donating

substituents (entries 10, 11, and 13 in Table 1) both can accelerate such a polar σ-bond metathesis. However, considering the fact that C-S bond formation of MeSMe took place from the Pt(IV) complex generated by the oxidative addition of MeI to [Pt(SMe)(PMe₂Ph)(μ-SMe)]₂,¹⁴ the route of path c cannot be fully ruled out, because the *trans* C-Pt-S geometry can be retained during the oxidative addition and following reductive elimination sequence.



Finally, the reaction of **2a** (0.12 mmol) with **6e** (0.1 mmol) and **7f** (0.1 mmol) in the presence of Pt(PPh₃)₄ (0.01 mmol) in toluene-*d*₈ (0.6 mL) was monitored by NMR spectroscopy at 105 °C (eq 7). The ³¹P NMR spectrum taken after 12 h showed the formation of a mixture of **1a** and **8a** in 78% and 5% yields based on Pt, respectively. On the other hand, its ¹H NMR spectrum detected the signals of 15% of **5g** and 5% of **4e**. Then the yields of **5g** and **4e** were increased gradually (26% and 9% after 24 h, respectively), while the yields of **1a** and **8a** hardly changed, indicating that the complexes **1** and **8** existed as resting states of the present Pt-catalyzed reaction. Judging from the foregoing experimental data, possible routes of the present Pt-catalyzed reaction of **2** with **6** and **7** are shown in Scheme 4.

Scheme 4. Possible Reaction Routes to **4** and **5** under the Pt-Catalyzed Reactions of **2** with **6** and **7**



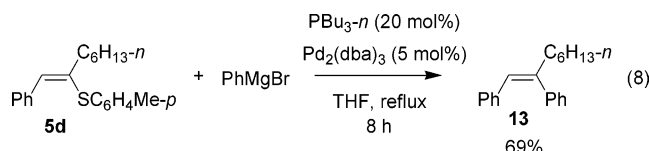
After the generation of **1** through the oxidative addition of **6** to Pt(0) and transmetalation with **7**,¹⁵ alkyne **2** would coordinate to **1** to produce **12**, whose formation can be the rate-limiting step of this Pt-catalyzed reaction. The coordinated alkyne may insert into the S-Pt bond to produce **3**, from which C-C bond-forming reductive elimination facily took place to give **5** with regeneration of Pt(0). When Ar is the aryl group, the complex **12** also competitively could react with **6** to give **8** and **4**, in the latter of which the Ar moiety was selectively incorporated from **6**. This could explain why the product distribution (**5/4**) was significantly influenced by the species of alkyne (**2**) and why the yields of **4f** and **8a**, **5g** and **8b**, **4e** and **8b**, and **5l** and **8a** in eqs 5 and 6 were comparable.

(13) The study of oxidative addition of vinyl sulfide to Pt(PPh₃)(C₂H₄) to yield vinyl platinum with a *cis*-sp²-C-Pt-S fragment supported that the sp²-C-S bond-forming reductive elimination was also a thermodynamically unfavorable process even from a *cis*-PPh₃-ligated isomer. Kuniyasu, H.; Ohtaka, A.; Nakazono, T.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2000**, *122*, 2375. See also ref 4.

(14) Puddephatt, R. J.; Upton, C. E. E. *J. Organomet. Chem.* **1975**, *91*, C17.

(15) The reaction of *trans*-Pt(Ph)(I)(PPh₃)₂ (**8c**, 0.01 mmol) with **7a** (0.1 mmol) in the presence of PPh₃ (0.1 mmol) in toluene (0.6 mL) produced *trans*-Pt(Ph)(SPh)(PPh₃)₂ (**1c**) and [Pt(Ph)(SPh)(PPh₃)₂]₂ (**1c'**) in 34% and 66% yields at 105 °C after 3 h, respectively.

Transformation of 5 into a Double Arylation Product. The utility of the present transformation was attested by converting the SAr group into an Ar group.^{2,3,16} The treatment of **5d** (0.5 mmol) with PhMgBr (1.0 mmol) in the presence of Pd₂(dba)₃·CHCl₃ (5 mol %) and PBu₃-*n* (20 mol %) under THF reflux for 8 h resulted in the formation of the desired (Z)-(Ph)(H)C=C(Ph)(C₆H₁₃-*n*) (**13**) in 69% yield (eq 8), enabling the introduction of two Ar groups into alkyne **2** by the sequential Pt-catalyzed carbothiolation and Pd-catalyzed cross-coupling reaction.



Conclusion

This study demonstrated that Pt-catalyzed carbothiolation of terminal alkyne with ArX and Ar'SM can be successfully realized by using 2- and 3-iodothiophene and Ar'SK. When aryl-I was employed as a coupling partner, the carbothiolation can significantly compete with C–S bond formation, where the participation of both alkyne and ArI was indicated. It must be emphasized that catalytic C–S bond-forming cross-coupling may take place through other than conventional direct C–S bond-forming reductive elimination from the M'(II) complex, suggesting that an alternative pathway must always be taken into account, when the mechanisms of a number of transition metal-catalyzed cross-coupling reactions of R–X with R'M are considered.¹

(16) Itami, K.; Mineno, M.; Muraoka, N.; Yoshida, J. *J. Am. Chem. Soc.* **2004**, *126*, 11778.

Experimental Section

General Procedures. ¹H and ¹³C NMR spectra in CDCl₃ solution and ³¹P NMR spectra in toluene-*d*₈ and benzene-*d*₆ solution were recorded with a JEOL JNM-Alice-400 (400 MHz). Chemical shifts in the ¹H NMR and ¹³C NMR spectra were recorded relative to Me₄Si and CDCl₃, respectively. Chemical shifts in the ³¹P NMR spectra were recorded relative to 85% H₃PO₄(aq) as an external standard. Infrared spectra were obtained with a Perkin-Elmer FT-IR (Model 1600). GC mass (EI) analyses were run using a Saturn GCMS-2000 spectrometer. Elemental analyses were performed in the Instrumental Analysis Center of the Faculty of Engineering, Osaka University. Preparative TLC was carried out using Wakogel B-5F silica gel using hexane and Et₂O as eluent. Toluene was distilled just before use. Aryl iodides, iodothiophene, PhSSn(Bu-*n*)₃, and alkynes were commercially available.

General Procedure of Pt-Catalyzed Arylthiolation of Alkynes 2 (entry 3 in Table 1). Into a 3 mL flask equipped with a reflux condenser were added Pt(PPh₃)₄ (62.2 mg, 0.05 mmol), PhSNa, (**7a**) (145.4 mg, 1.1 mmol), toluene (0.5 mL), PhI (**6c**) (204.0 mg, 1.0 mmol), and 1-octyne (**2a**) (132.2 mg, 1.2 mmol). The reaction mixture was vigorously refluxed for 24 h under a nitrogen atmosphere, the resulting mixture was filtrated through Celite, and the resultant filtrate was evaporated. The products (**5a**) were isolated by PTLC (eluent: hexane and ether) (83% yield). Other reactions in Table 1 were performed similarly. In the cases of entries 8–13, 1.0 mL of toluene was used as the solvent.

Attempted Reductive Elimination of 4e from 1a (eq 2). Into a dry Pyrex NMR tube were added **1a** (9.5 mg, 0.01 mmol), PPh₃ (13.1 mg, 0.05 mmol), and toluene-*d*₈ (0.6 mL) under N₂ atmosphere. Then the reaction at 110 °C was monitored by NMR spectroscopy. However, no formation of **4e** was observed even after 20 h. Other mechanistic studies shown in eqs 3–7 were performed similarly.

Supporting Information Available: Experimental procedures and spectral data of the products and authentic **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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